

IN-90-CR
87800

ANNUAL REPORT

**Experimental Studies of Nucleation and Growth
Processes Related to the Formation of Presolar Grains**

P.7

GRANT NAG 5-1494

To

Astrochemistry Branch
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May 15, 1992

(NASA-CR-185481) EXPERIMENTAL STUDIES OF
NUCLEATION AND GROWTH PROCESSES RELATED TO
THE FORMATION OF PRESOLAR GRAINS Annual
Report (Calvert Inst.) 7 p

N92-25729

Unclass
G3/90 0087800

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Abstract

This research is in support of experimental research in the Astrochemistry Branch of the Laboratory for Extraterrestrial Physics at Goddard Space Flight Center. The research is directed toward understanding the mechanisms of nucleation of refractory materials, and the relative importance of factors controlling the rate of cluster formation and growth for astrophysically important species. The structure and composition of the condensates is being investigated, with the goal of characterizing the grains present in the primitive solar nebula.

1. Introduction

A significant research effort is underway in the Astrochemistry Branch at Goddard Space Flight Center to elucidate the mechanisms responsible for the formation and evolution of presolar grains. This experimental effort involves both cluster beam experiments and high temperature flow tube experiments. In addition, microgravity nucleation experiments are being performed using a NASA KC-135 research aircraft, to minimize settling out of larger particulates during laboratory experiments.

The purpose of the present research is to support several research activities at Goddard. This report covers the period from February 1, 1991 to January 31, 1992. Ongoing tasks involve studies of the morphology, composition and structure of mixed oxide condensates; non-mass dependent oxygen isotope fractionation; vapor-phase hydration of refractory smoke; and production of metal-carbonaceous smokes.

Pre-solar dust grains were the chief source of opacity in the early stages of nebular collapse: reprocessed or recondensed phases may have been important sources of opacity during later stages of nebular evolution. The dust grains carry all surviving records of astrophysical nucleosynthetic events which may have triggered the collapse of the giant molecular cloud which formed the sun and planets. The morphology, composition, crystal structure and spectral properties of both pre-solar grains as well as those formed in the nebula will determine the temperature profile of the disk, the grain-grain sticking probability (the first stage in the growth of planets), the volatile and noble gas content of planetesimals and the isotopic compositions of comets, asteroids, planets and their atmospheres.

The primary vapor-phase species for refractory metals under "natural" conditions are SiO, AlO, Mg and Fe. Nucleation and growth of grains from such a gas will yield an underoxidized product compared with the solids predicted from thermodynamics calculations even if some

oxygen is incorporated into the growing grains via reaction with O, OH or H₂O. The result of this disequilibrium will be a series of oxidation-reduction reactions within the grain as a consequence of virtually any type of energetic processing: thermal annealing, photon/cosmic ray heating, hydration, etc. One consequence of this internal oxidation/reduction couple will be the initial reduction of some SiO by AlO resulting in very little opacity at 20 μ and a reduction in the expected grain opacity at 10 μ due to a reduction in the number of SiO bonds.

Similarly, the opacity from approximately 1-3 μ is a very sensitive function of the overall oxidation state of the grain. Fe⁺² absorbs strongly between 1-3 μ while Fe⁰ and Fe⁺³ do not absorb at all in the infrared. SiO will reduce Fe⁺³ to Fe⁺² but will also reduce Fe⁺² to Fe⁰: if Fe⁰ can segregate into a metallic phase then it may be resistant to oxidation or hydration on short timescales. Because a 1000-3000K blackbody has its peak emission between 3-1 μ (respectively) the precise oxidation state of iron is likely to be an extremely important unknown in any estimate of the opacity of the nebular disk.

The following two sections briefly outline the scope of the tasks comprising the direction of current research, and present a draft of a paper resulting from our laboratory studies of small iron grains.

2. Outline of Research Tasks.

This research involves continuing experimental studies of nucleation phenomena related to understanding the growth characteristics of interstellar grains. The research program divided into four tasks as described below.

Task 1. Morphology, Composition and Structure of Mixed Oxide Condensates

Previous research carried out in the astrochemistry branch, with collaboration from Dr. Reitmeijer at the University of New Mexico, has shown that the initially homogeneous gas mixtures in the graphite furnace produces particles that are very heterogeneous: large coalesced blobs of silica; small Al-SiO, Fe-SiO or Al-Fe-SiO particles which coagulate into an open, fluffy morphology in which the grains of similar composition appear to cluster together; and core-mantle grains (iron oxide cores with silica mantles). The size distribution of the different grain populations are dominated by different Ostwald Ripening kinetics and appear to indicate differential, compositionally controlled nucleation and growth. This task is composed of the following investigations:

- Synthesis of particles from bulk gas mixtures in widely varying regions of the Fe-Al-Si phase diagram.

- Annealing the particles in the hot stage of the TEM at 1000K and following the kinetics of the annealing/crystallization process.

These experiments permit us to observe and gain an understanding of the phase changes in terms of oxidation/reduction processes acting in individual grains.

Task 2. Non-mass Dependent Oxygen Isotopic Fractionation

Previous experiments (in collaboration with Professor Thiemens at UCSD) have shown a non-mass dependent oxygen isotopic fractionation during the condensation of metal oxide smokes from a vapor containing oxygen atoms. Experiments performed to date have made no effort to reduce oxidation of the original condensates by residual flow gas, atmospheric oxygen or water vapor. Such contaminants may have significantly diluted the anomalous oxygen component present in our original samples. The following experiments are planned to determine the extent to which oxidation of growing grains influences the effect we observe:

- Collect samples of the materials directly from the flow stream, transferring them under dry nitrogen to UCSD for analysis.
- Study nucleation using both He and H₂ carrier gases to see if oxidation of growing grains by OH might dilute the observed non-mass dependent effect.

Differential nucleation may enhance the non-mass dependent fractionization and produce separate phases incorporating various amounts of anomalous oxygen. If we observe an enhancement of the effect in our bulk grains (e.g., by elimination of contaminants) to the point where measurements using the ion microprobe are feasible, the following experiment will be performed:

- Use a mixture of metal precursors plus N₂O in H₂ and send the resulting nucleated samples to Professor Zinner at Washington University for ion microprobe analysis.

Task 3. Vapor-phase Hydration of Refractory Smoke

We have previously determined the rate constant and activation energies for hydration of silicate smokes by liquid water and these results have been applied to estimate the rate of grain processing in comets and primitive meteorites. The recently acquired Parr Reactor enables the extension of these studies to higher temperatures and pressures. Such studies are necessary if we are to adequately model possible hydration reactions which may have occurred over longer timescales at lower water vapor pressures in the primitive solar nebula. Specifically, we will

- Measure the hydration rate as a function of temperature and pressure, independently varying both temperature and pressure.

Task 4. Production of Metal-Carbonaceous Smokes

Some of the most interesting work in recent years is the recovery of presolar carbonaceous grains from meteorites and the relationship of such materials to the interstellar grain population. We are studying metal smokes in a carbon-rich atmosphere ($C/O > 1$) by adding sufficient C_2H_2 to our gas flow stream to balance (or overwhelm) the oxygen added to the mixture. The composition of the smoke depends on the details of the various reaction pathways in the gas phase and on the temperature of the furnace. We are attempting to determine the crystal structure, spectral properties, morphology and size distributions of the grains which form.

3. Laboratory studies of small iron grains

Iron grains on the order of 20 nanometers in diameter have been produced in the Condensation Flow System (1) at GSFC. They were formed from Iron Pentacarbonyl vapor in a molecular hydrogen flow at a total pressure of 100 torr and furnace temperatures between ~500 K and 1300 K. Particulates were formed both in the presence and absence of a magnetic field. The strength of the magnetic field to which the freshly nucleated particles were exposed was on the order of 100 gauss and was generated by the AC current (~1000 Amps) flowing through our furnace. In the absence of a magnetic field (we turned off the furnace before the flow began) the 20 nm particles slowly settled out of the hydrogen carrier gas and were deposited on glass collection surfaces. Nothing unusual was observed in these experiments. However, in the presence of a magnetic field an extremely unusual phenomenon was observed to occur: although the particulates would initially be carried along with the hydrogen flow for the first few seconds of the experiments, they would suddenly gel into a mass of dense "spiderwebs". At very low particle concentrations we observed the formation of long "streamers" floating gently in the hydrogen flow or hanging from the walls of our chambers a few minutes after the iron carbonyl vapor began to flow through the furnace.

Measurements of the magnetic remnance acquired by macroscopic samples of these iron spiderwebs indicate that they are magnetically oriented and magnetized to a few percent of the saturated remnance. SEM studies of the samples reveal very long strands consisting of hundreds of single particles connected head-to-tail and which are intertwined into a very low density mass of fibers. TEM images of single strands reveal ~20 nanometer diameter oxide-coated, iron particles connected at an average angle of $\sim 108^\circ \pm 45^\circ$ or so. The evidence appears to indicate that the

fibers. TEM images of single strands reveal ~20 nanometer diameter oxide-coated, iron particles connected at an average angle of $\sim 108^\circ \pm 45^\circ$ or so. The evidence appears to indicate that the particle coagulated in an oriented fashion, pole-to-opposite pole. Given that such large-scale structures have never been observed in other grains condensed in the Condensation Flow System and that even iron grains do not form such structures in the absence of a strong field it is obvious that this remnant magnetism greatly increases the coagulation efficiency of iron. This increase in the coagulation efficiency may result from increased cohesiveness of colliding grains, or, more likely, to longer range interaction forces which increase the effective collision radii of the grains.

These experiments may be relevant to the early solar nebula for the following reasons. One possible mechanism by which chondrules are hypothesized to form in the solar nebula is as the result of nebular lightning strokes heating large volumes of dusty metallic gas to very high temperatures for very short times. (2) As the chondrules form they lose metallic iron - possibly either as small molten metal grains which are centrifugally expelled from spinning chondrules or as iron vapor which could quickly recondense. If recondensation or cooling through the Curie point occurs in the presence of the lightning discharge, or if such a grain is later exposed to a strong magnetic field following a second discharge then this imprinted magnetic field would greatly increase the coagulation efficiency of such grains. Because these grains tend to form very loose, open, fibrous structures they could act as "nets" or coagulation nuclei to catalyze formation of larger aggregates of non-magnetic materials which may have become the meteorite matrix. Unfortunately, since these iron nets consist of particles on ~20 nm in diameter they would be extremely susceptible to oxidation in the matrix. It is not yet clear if a definitive test for the remnants of such grains in meteoritic matrix exists; however close associations of magnetite grains in meteorite matrix - especially if such grains are coherently magnetized - could be one indication that such a mechanism operated in the solar nebula.

References:

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Acknowledgment

This work was performed at Goddard Space Flight Center in the Astrochemistry Branch, Laboratory for Extraterrestrial Physics. It was performed in association with Joseph Nuth, J. Faris and P. Wasilewski.